Triphenylphosphine/Dichloroselenurane: A New Reagent for a Selective Conversion of Alcohols into Alkyl Chlorides

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Alkyl chlorides are commonly used as both very useful synthetic intermediates and valuable end products.[1] Among numerous methods of their preparation, the most important is the conversion of alcohols into alkyl chlorides.[2,3] The best reagents for such a displacement of the hydroxy group by chlorine are organophosphorus compounds such as PCl_5, R_3PCl_2, or the Ph_3P/CCl_4 system, called the Appel reagent. Usually, the reactions of alcohols with these reagents occur with a high efficiency, under mild and neutral conditions. However, some of them were found to give products with the rearranged carbon skeleton (the case of allylic alcohols) or extensively racemized when optically active alcohols are used.[4] Therefore, there is a continuous search for new reagents and improved preparative procedures allowing efficient conversion of alcohols into alkyl halides.[5]

In the course of our wider study on the application of heteroorganic compounds in organic synthesis,[6] we have found a new reagent system for converting alcohols into chlorides that avoids the shortcomings mentioned above. It was found that the easily available dimethyldichloroselenurane (**1a**) as well as diphenyldichloroselenurane (**1b**) (see the Experimental Section) react with alcohols **2** in the presence of equimolar amounts of triphenylphosphine leading to the clean formation of the corresponding chlorides **3**. The overall reaction is shown in eq 1.

$$R^1OH + R_2^2SeCl_2 + PPh_3 \longrightarrow R^1Cl + Ph_3PO + R_2^2Se + HCl \quad \text{(eq. 1)}$$

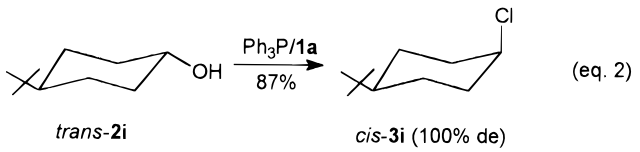
2 **1a**, R^2=Me; **1b**, R^2=Ph **3**

Table 1. Reaction of Alcohols, ROH 2, with Triphenylphosphine/Dichloroselenurane 1 System

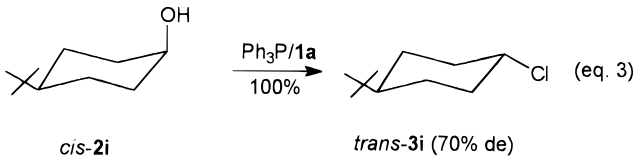
	alcohol **2**					
		dichloro-		time	yield of **3** (%)	
no.	R	selenurane	solvent	(min)	GLC	isolated
a	*n*-C_8H_{17}	**1a**	$CHCl_3$	20	100	100
a	*n*-C_8H_{17}	**1b**	C_6H_6	20		100
b	*n*-$C_{12}H_{25}$	**1a**	C_6H_6	60	99	92
c	$C_6H_5CH_2$	**1a**	$CHCl_3$	20	99	89
d	*o*-$CH_3OC_6H_4CH_2$	**1b**	CH_2Cl_2	20	100	95
e	*m*-$CH_3OC_6H_4CH_2$	**1b**	CH_2Cl_2	20	100	95
f	$C_6H_5CH_2CH_2$	**1b**	CH_2Cl_2	20	100	95
g	$C_6H_5(CH_3)CH$	**1a**	$CHCl_3$	10	100	95
h	$C_6H_5CH{=}CHCH_2$	**1a**	C_6H_6	2 days	95	66
i	4-*t*-Bu-cyclo-C_6H_{10}[a]	**1a**	$CHCl_3$	20	99	92
j	adamantyl	**1a**	C_6H_6	10		93

[a] A 7:3 mixture of trans and cis isomers.

The reaction of alcohols **2** dissolved in an inert solvent (dichloromethane, chloroform, benzene) with 1 equiv of Ph_3P/Me_2SeCl_2 is rapid and exothermic. Removal of the solvent, dimethyl selenide, and hydrogen chloride by evaporation under reduced pressure and triphenylphosphine oxide by rapid chromatography affords virtually pure chlorides **3**. The scope of this reaction was investigated on a number of primary, secondary, and tertiary alcohols. Table 1 displays the relevant data whose salient features are as follows: (a) The reaction conditions are much milder than those using Ph_3P/CCl_4[4b] or Ph_3PCl_2[4e] as reagents; the latter typically reacts with alcohols at room temperature for 1−2 days or at 50−80 °C for several hours. (b) The yields of **3** are very high, and in many cases, the crude reaction products can be used without further purification. An advantage of the present methods is well demonstrated by the synthesis of 4-*tert*-butylcyclohexyl chloride **3i** obtained in over 90% yield. An alternative and commonly used synthetic procedure[7] involving treatment of **2i** with thionyl chloride in the presence of an equimolar amount of tri-*n*-butylamine affords the desired chloride **3i** in yield lower than 20% and accompanied by comparable amounts of **3**-*tert*-butylcyclohexene. (c) The carbon−carbon double bond



trans-**2i** *cis*-**3i** (100% de) (eq. 2)



cis-**2i** *trans*-**3i** (70% de) (eq. 3)

geometry is fully preserved in the unrearranged product (see cinnamyl chloride **3h**). (d) There are no elimination

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(1) (a) *The Chemistry of the Carbon-Halogen Bond*; Patai, S., Ed.; John Wiley & Sons: Chichester, 1973; Parts 1 and 2. (b) *Supplement D: The Chemistry of halides, pseudohalides and azides*; Patai, S., Ed.; John Wiley & Sons: Chichester, 1983. (c) Larock, R. C. *Comprehensive Organic Transformations*; VCH: Weiheim, 1994; pp 354−363.

(2) Bohlmann, R. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 6, pp 203−223.

(3) Reference 1b, pp 1021−1173.

(4) (a) Magid, R. M.; Fuchey, O. S.; Johnson W. J. *Tetrahedron Lett.* **1997**, 2999. (b) Slage, T. T.; Huang, T. T.-S.; Franzus, B. *J. Org. Chem.* **1978**, *46*, 3526. (c) Jones, L. A.; Sumner, C. E., Jr.; Franzus, B.; Huang, T. T.-S.; Snyder, J. *J. Org. Chem.* **1978**, *43*, 2811. (d) Magid, R. M.; Fuchey, O. S.; Johnson, W. J.; Allen, T. G. *J. Org. Chem.* **1979**, *44*, 361. (e) Garegg, P. J.; Johansson, R.; Samuelsson, B. *Synthesis* **1984**, 168.

(5) (a) Rivero, I. A.; Somanthan, R.; Hellberg, L. H. *Synth. Commun.* **1993**, *23*, 711. (b) Snyder, D. C. *J. Org. Chem.* **1995**, *60*, 2638. (c) Frøyen, P.; Juvvik, P. *Phosphorus, Sulfur, Silicon* **1996**, *116*, 217. (d) Tanaka, A.; Oritani, T. *Tetrahedron Lett.* **1997**, *38*, 1955. (e) Leonel, E.; Paugam, J. P.; Nedelec, J. Y. *J. Org. Chem.* **1997**, *62*, 7061.

(6) For recent reviews, see: Mikołajczyk, M. *South Af. J. Chem.* **1994**, *47*, 103. Drabowicz, J., Łuczak, J.; Łyżwa, P.; Mikołajczyk, M. *Phosphorus, Sulfur, Silicon*, in press.

(7) (a) Greene, F. D.; Chu, C. C.; Walra, J. *J. Org. Chem.* **1964**, *29*, 1285. (b) Giese, B.; Harung, J.; Kesselheim, C.; Lindner, H. J.; Svoboda, I. *Chem. Ber.* **1993**, *126*, 1193.

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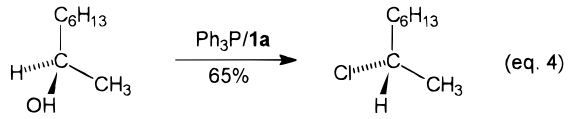
byproducts in the reaction with α-phenylethanol **2g** and adamantol **2j**.

Several families of alcohols were investigated in order to determine the scope of the reaction. The usefulness of the new method for conversion of alcohols into chlorides was demonstrated by experiments with optically active substrates. Thus, both enantiomers of 2-octanol **2k** and (−)-menthol **2l** were selected as representative chiral saturated alcohols, as was (−)cholesterol **2m**, which contains an unsaturation. This choice was dictated mainly by the fact that its conversion into the corresponding chloride gives always the levorotatory cholesteryl chloride with retained configuration at the reactive center.[8] Moreover, the steric course of the reaction was investigated using *cis*- and *trans-tert*-butylcyclohexanols **2i** as cyclic model alcohols.[9]

It was found that *trans*-**2i** was converted stereospecifically into *cis*-**3i** upon treatment with the Ph_3P/**1a** reagent system, while the reaction with *cis*-**2i** gave a 85:15 mixture of *trans*- and *cis*-**3i**, respectively.[10] These results clearly indicate that the cyclic chlorides **3i** are formed with inversion of configuration, although its extent is dependent on the stereochemistry of the substrate used.

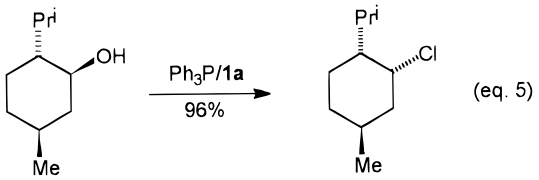
In the case of acyclic, chiral alcohols, both enantiomers of **2k** and (−)-**2l** were converted to the corresponding chlorides **3k** and **3l** with essentially full inversion of configuration (eqs 4 and 5).



(eq. 4)

(-)-(*R*)-**2k**, $[\alpha]_D$= - 7.1 (72% ee) (+)-(*S*)-**3k**, $[\alpha]_D$= +26.1[11]

(+)-(*S*)-**2k**, $[\alpha]_D$=+7.9 (79.9% ee) (-)-(*R*)-**3k**, $[\alpha]_D$= - 27.1[11]

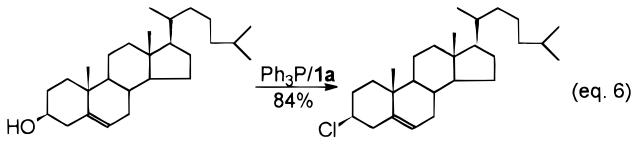


(eq. 5)

(1*R*, 2*S*, 5*R*)-**2l** (1*S*, 2*S*, 5*R*)-**3l**

$[\alpha]_D$= - 50.5 (100% ee) $[\alpha]_D$= +57.2 (100% ee)[13]

On the contrary, (−)-cholesterol **2m** was converted into the corresponding chloride **3m** with full retention of configuration (eq 6).[15] Thus, the stereochemical outcome of the reaction under discussion is similar to those observed with other reagents and is due to the S_N1 mechanism involving the participation of the homoallylic carbonium ion.[8f]



(eq. 6)

(-)-**2m**, $[\alpha]_D$= - 40.2 ($CHCl_3$) (-)-**3m**, $[\alpha]_D$= - 31.2 ($CHCl_3$)

To gain insight into the reaction mechanism, or the pathway of the reaction, the nature of our reagent system, Ph_3P/Ph_2SeCl_2, was first studied by means of the ^{31}P and ^{77}Se NMR spectroscopy. Thus, a solution of Ph_3P in CH_2Cl_2 was treated with an equimolar amount of Ph_2SeCl_2, **1b**, and the resulting mixture was examined by ^{31}P NMR $\{^1H\}$ (81 MHz) with proton noise decoupling. A single resonance signal was observed at $\delta_P = 56$ ppm, which upon addition of *tert*-butyl alcohol disappeared and a new signal at $\delta_P = 31.5$ ppm was cleanly formed. Similarly, a mixture of Ph_3P and Cl_2 in CH_2Cl_2 showed one signal at $\delta_P = 65$ ppm. Addition of *tert*-butyl alcohol to this solution caused disappearance of the latter, and appearance of a new signal at $\delta_P = 37$ ppm became visible. In view of the literature data,[18] the signals at $\delta_P = 56$ and 65 ppm can be attributed to a triphenylchlorophosphonium cation and those resonating at $\delta_P = 31.5$ and 37 ppm to *tert*-butoxyphosphonium cation formed. The differences in chemical shifts observed for both phosphonium cations are due to a specific counterion effect, which will be discussed later. However, a different set of results was observed in toluene. The $^{31}P\{^1H\}$ NMR spectrum of the same reagent mixture, Ph_3P/Ph_2SeCl_2, showed sharp singlet at $\delta_P = -46.6$ ppm. This value is typical of pentacoordinate phosphorus compounds,[19] and therefore, this signal may be ascribed to triphenyldichlorophosphorane. Interestingly, a mixture of Ph_3P and Cl_2 in toluene showed a signal at $\delta_P = 64$ ppm. This indicates the existence of triphenylchlorophosphonium cation in both solvents. However, when diphenyl selenide was added to this mixture in toluene, the signal at $\delta_P = 64$ ppm disappeared and the signal at $\delta_P = -47$ ppm appeared, thus demonstrating the formation of the P^V structure.

In contrast to ^{31}P NMR spectra, the ^{77}Se NMR chemical shifts of our reagent system in CH_2Cl_2 and toluene were found to be very similar ($\delta_{Se} = 415.8$ ppm in CH_2Cl_2 and 417.7 ppm in toluene). The ^{77}Se NMR spectra of diphenyldichloroselenurane, **1b**, itself in CH_2Cl_2 and toluene displayed also very close resonance signals at $\delta_{Se} = 576.95$ and 568.3 ppm, respectively. Last, it should be

(8) (a) Planer, A. *Ann.* **1861**, *118*, 25. (b) Loebisch, R. *Chem. Ber.* **1872**, *5*, 310. (c) Diels, O.; Blumberg, P. *Chem. Ber.* **1911**, *44*, 2847. (d) Doughensbaugh, T.; Allison, F. *J. Am. Chem. Soc.* **1929**, *51*, 3665. (e) Shoppee, C. W. *J. Chem. Soc.* **1946**, 1147. (f) Simonetta, M.; Winstein, S. *J. Am. Chem. Soc.* **1954**, *76*, 18.

(9) The commercially available mixture of diastereomers (cis/trans ratio = 3:7) was resolved into pure components by preparative HPLC chromatography. They show characteristic absorptions for the methine proton connected with the hydroxyl group [for *cis*-**2i** $\delta = 4.037$ ppm (quintet) and for *trans*-**2i** $\delta = 3.57$ ppm (nine lines)].

(10) Assignment of configuration to the chlorides **3i** was based on the chemical shift of the proton at C1 in the ^1H NMR spectra ($\delta = 4.49$ ppm for *cis*-**3i**; $\delta = 3.79$ ppm for *trans*-**3i**). These values are somewhat different from those reported in ref 7a ($\delta = 4.27$ ppm for *cis*-**3i** and $\delta = 3.64$ ppm for *trans*-**3i**).

(11) In view of our results, the highest optical rotation reported for **3k**, $[\alpha]_D = -31.6$ (MeOH),[12] does not correspond to optically pure chloride. Assuming full inversion in our reaction its value should be equal to $[\alpha]_D = 36.25$ (MeOH).

(12) Chaudri, B. A.; Goodwin, D. G.; Hudsono, H. R.; Bartlett, L.; Scopes, P. M. *J. Chem. Soc. C* **1970**, 1329.

(13) The highest value of optical rotation reported for dextrorotatory menthyl chloride **3l** is equal to $[\alpha]_D = +52.0$ ($CHCl_3$).[14]

(14) Smith, J. G.; Wright, G. F. *J. Org. Chem.* **1952**, *17*, 1116.

(15) The highest value of optical rotation, $[\alpha]_D = -30.0$ ($CHCl_3$), for (−)-cholesteryl chloride was reported by Barton and Cox.[16] The chloride **3m** prepared by the reaction of (−)-cholesterol and thionyl chloride had mp 95.5−96.5 °C.[17]

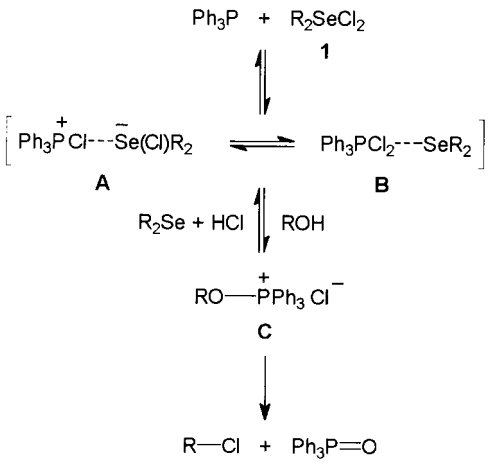
(16) Barton, D. H.; Cox, J. D. *J. Chem. Soc.* **1948**, 783.

(17) Winstein, S.; Kossower, E. M. *J. Am. Chem. Soc.* **1959**, *81*, 4399.

(18) Grochowski, E.; Hilton, B. D.; Kupper, R. J.; Michejda, C. J. *J. Am. Chem. Soc.* **1982**, *104*, 6872.

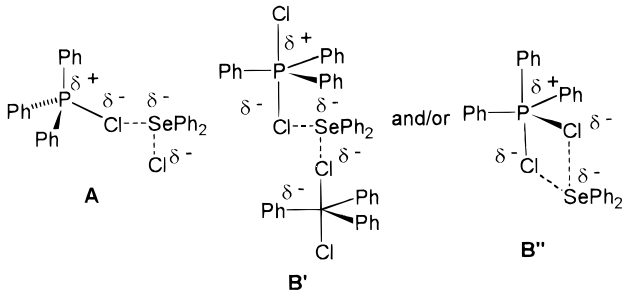
(19) In their recent paper, Godfrey et al. reported the $\delta_P = -47$ ppm for Ph_3PCl_2 in deuterated benzene: Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G.; Sheffield, J. M. *J. Chem. Soc., Chem. Commun.* **1998**, 921.

Scheme 1



emphasized that in the phosphorus and selenium NMR spectra of a mixture Ph_3P and Ph_2SeCl_2 no coupling between the two hetero nuclei was observed.

The results of spectroscopic studies of our reagent system are best rationalized in terms of an equilibrium between the salt **A** and the phosphorane **B**, which is shifted toward the salt **A** in CH_2Cl_2, while in toluene the structure **B** is strongly preferred. In both equilibrium components, the phosphorus and selenium counterparts are interacting with each other. In the salt **A** the chlorophosphonium cation is most probably involved in interaction with the selenurane anion via the chlorine atom. Since the selenium chemical shifts for **A** and **B** are practically the same, the chemical environment around selenium in both structures should be the same. This requirement is fulfilled when the salt **A** and phosphorane **B** adopt the structures depicted below. Further structural studies of **A** and **B**, which are beyond the scope of this work, are in progress.

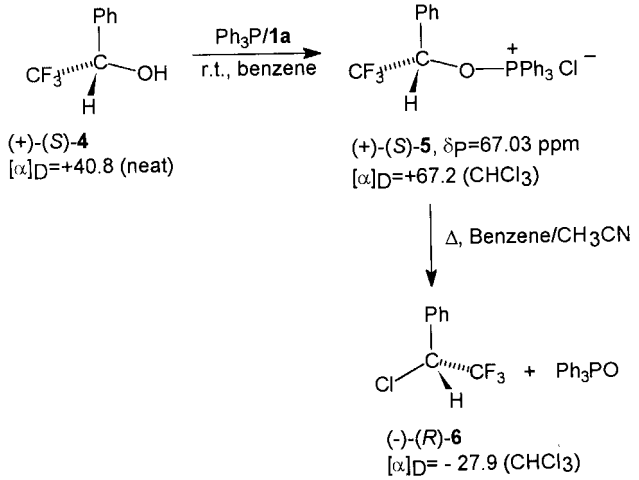


The next step of the reaction under discussion involves nucleophilic attack of an alcohol on the phosphorus in the salt **A** leading to the alkoxyphosphonium salt **C**, which in the final step undergoes decomposion to alkyl chloride with inversion of configuration (see Scheme 1).

In addition to ^{31}P NMR evidence supporting such a reaction course, we were able to isolate and fully characterize the phosphonium salt **5** formed in the reaction between (+)-(*S*)-α-(trifluoromethyl)benzyl alcohol **4** and the mixed reagent PPh_3/**1a** (Scheme 2). This salt underwent slow conversion to the corresponding chloride **6** and triphenylphosphine oxide upon heating in a boiling mixture of benzene−acetonitrile (1:1).

In summary, we have described here a very efficient, stereoselective synthesis of alkyl chlorides from alcohols using a mixture of triphenylphosphine and dimethyl- or diphenyldichloroselenurane as reagent system. Dichloroselenurane plays a dual role in this reaction. It transfers chlorine to phosphorus as well as facilitating substitution of chlorine by alkoxy group in chlorophosphonium salt formed as an intermediate. Application of the described method for the ROH to RCl conversion in carbohydrates and nucleosides is under current study.

Scheme 2



Experimental Section

General Procedures. Melting points are not corrected. ^1H NMR spectra were recorded on 200 or 300 MHz instruments. ^{31}P NMR spectra were obtained on a 200 MHz spectrometer in the Fourier transform mode at 81 MHz. ^{77}Se NMR spectra were measured on a 300 MHz spectrometer in the Fourier transform mode at 57 MHz. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane for ^1H nuclei, from external phosphoric acid for ^{31}P nuclei, and from external diphenyldiselenide for ^{77}Se nuclei. Analytical VPC work was accomplished using a gas chromatograph with the DB-1 capillary column (length 30m). Preparative HPLC separations were done on a standard silica gel 10 μm column. All elemental analyses were performed by the Analytical Laboratory of the Center of Molecular and Macromolecular Studies, PAS.

Sulfuryl chloride used was a commercial product distilled over sulfuric acid immediately before use. Triphenylphosphine was recrystallized prior to use. All alcohols used were commercial products purified before use according to the standard procedures. Dimethyl selenide was prepared by the exhaustive methylation with methyl bromide of sodium selenide generated in situ by the reduction of elemental selenium with rongalite.[20] Diphenyl selenide was prepared by the high-temperature reaction of diphenyl sulfone with elemental selenium.[21]

Caution! In the absence of toxicity data, the selenium compounds should be treated as though they were toxic materials. Therefore, the preparations of dimethyl and diphenyl selenides and all the operations with them should be carried out in a well-wentilated hood. Rubber gloves should be worn by the operator to avoid the contact of the skin with these materials.

Dimethyldichloroselenurane (1a). To a stirred solution of dimethyl selenide (3.76 g, 20 mmol) in ethyl ether (20 mL) was added dropwise sulfuryl chloride (2.70 g, 20 mmol) at 0 °C. Stirring was continued for an additional 15 min. The crystals formed during addition of sulfuryl chloride were filtered off, washed with anhydrous benzene, and dried under reduced pressure to give the analytically pure product **1a** (5.82 g, 100%): mp 46−49 °C; ^1H NMR ($CHCl_3$) δ 3.612, J_{H-Se} = 10.165 Hz; ^{13}C NMR ($CHCl_3$) δ 44.70; ^{77}Se NMR ($CHCl_3$) δ 449.14.

Anal. Calcd for $C_2H_6Cl_2Se$: C, 13.33; H, 3.33. Found: C, 13.29; H, 3.58.

(20) Bird, M. L.; Chalanger, F. *J. Chem. Soc.* **1942**, 571.
(21) Krafft, F.; Lyons, R. E. *Chem. Ber.* **1884**, *27*, 1761.

Diphenyldichloroselenurane (1b). This selenurane was prepared in a quantitative yield according to the above-described procedure: mp 161−162 °C; ^{1}H NMR ($CHCl_3$) δ 7.52−7.58 and 8.00−8.04 m); ^{13}C NMR ($CHCl_3$) δ 129.673, 131.285, 131.662, 142.410; ^{77}Se NMR ($CHCl_3$) δ 574.86.

Anal. Calcd for $C_{12}H_{10}Cl_2Se$: C, 47.36; H, 3.28. Found: C, 47.40; H, 3.64.

General Procedure for Reaction of Achiral Alcohols 2. In a 10 mL flask, **2** (1 mmol) and triphenylphosphine (1 mmol) were dissolved in the appropriate solvent (3 mL). To a clear solution was added the dichloroselenurane **1a** or **1b** (1 mmol) in small portions over a few minutes. When the addition of the dichloroselenurane was completed, the solvent was removed under reduced pressure, and hexane (10−15 mL) was added to the residue. The precipitated triphenylphosphine oxide was filtered off. To remove remaining traces, the hexane solution was passed through a short silica gel column. Removal of the solvent gave virtually pure chloride **3**, the purity of which was checked by GC, and the structure was supported by the analysis of its ^{1}H NMR spectra.

(a) *o*-Methoxybenzyl chloride (**3d**): ^{1}H NMR ($CDCl_3$) δ 3.9 (s, 3H), 4.7 (s, 2H), 6.9−7.05 and 7.25−7.45 (m, 4H).

(b) *m*-Methoxybenzyl chloride (**3e**): ^{1}H NMR ($CDCl_3$) δ 3.8 (s, 3H), 4.57 (s, 2H), 6.85−7.0 (m, 4H).

(c) 2-Chloro-1-phenylethane (**3f**): ^{1}H NMR ($CDCl_3$) δ 3.1 (t, 2H), 3.75 (t, 2H), 7.25−7.60 (m, 5H).

(d) 1-Chloro-1-phenylethane (**3g**): ^{1}H NMR ($CDCl_3$) δ 1.9 (d, 3H), 5.15 (q, 1H), 7.30−7.50 (m, 5H).

Reaction of Cyclic Alcohols. *cis*-4-*tert*-Butylcyclohexanol (2i). To a solution of *cis*-**2i** (0.056 g, 0.359 mmol) and triphenylphosphine (0.095 g, 0.362 mmol) in methylene chloride (5 mL) was added dimethyldichloroselenurane (**1a**) (0.095 g, 0.36 mmol) in small portions over 10 min. The resulting solution was left for 20 min at room temperature. After that time, petroleum ether (10 mL) and solid sodium carbonate (0.050 g) were added, and the precipitated triphenylphosphine oxide was filtered off. After removal of the solvent, the liquid residue was subjected to chromatography on silica gel using pentane as eluent to yield a mixture of *trans*- and *cis*-4-*tert*-butylcyclohexyl chloride (**3i**) (85:15): 0.054 g (87%); ^{1}H NMR ($CDCl_3$) δ 0.863 (s, 9H), 1.423−2.255 (m, 9H), 3.790 and 4.490 (m, 1H).

***trans*-4-*tert*-Butylcyclohexanol (2i).** To a solution of *trans*-**2i** (0.057 g, 0.365 mmol) and triphenylphosphine (0.097 g, 0.37 mmol) in methylene chloride (5 mL) was added dimethyldichloroselenurane (**1a**) (0.067 g, 0.36 mmol) in small portions over 10 min. The resulting solution was left for 20 min at room temperature. After that time, petroleum ether (10 mL) and sodium carbonate (0.050 g) were added, and the precipitated triphenylphosphine oxide was filtered off. After removal of the solvent, the liquid residue was subjected to chromatography on silica gel using pentane as eluent to yield pure *cis*-4-*tert*-butylcyclohexyl chloride **3i**: 0.062 g (99%); ^{1}H NMR ($CDCl_3$) δ 0.886 (s, 9H), 1.415−2.15 (m, 9H), 4.490 (m, 1H).

Reaction of Optically Active Alcohols. (−)-(*R*)-2-Octanol (2k). To a solution of (−)-(*R*)-**2k** [0.13 g, 1 mmol; $[\alpha]_{589} = -7.17$ (neat) (ee = 72%)] and triphenylphosphine (0.262 g, 1 mmol) in benzene (5 mL) was added dimethydichloroselenurane (**1a**) (0.18 g, 1 mmol) in small portions over 10 min. The resulting solution was left for 4 h at room temperature. After that time, pentane (10 mL) was added, and the precipitating triphenylphosphine oxide was filtered off. After removal of the solvent, the liquid residue was subjected to chromatography on silica gel using hexane as eluent to yield the pure (+)-(*S*)-2-octyl chloride (**3k**) 0.095 g (64%); $[\alpha]_{589} = +26.1$ (c = 9.0, MeOH).

(+)-(*S*)-2-Octanol (2k). A similar procedure using (+)-(S)-**2k**, $[\alpha]_{589} = +7.9$ (neat) (ee = 79.9%), yielded (−)-(R)-2-octyl chloride (**3k**) in a comparable yield: $[\alpha]_{589} = -27.03$ (c = 4, MeOH).

(−)-(1*R*,2*S*,5*R*)-Menthol (2l). To a solution of (−)-**2l** [0.156 g, 1 mmol, $[\alpha]_{589} = -50.5$ (c = 1.00 EtOH) (ee = 100%)] and triphenylphosphine (0.262 g, 1 mmol) in benzene (3 mL) was added dimethyldichloroselenurane (0.18 g, 1 mmol) in small portions over 10 min. The resulting solution was left for 24 h at room temperature. After that time, pentane (10 mL) was added, and the precipitating triphenylphosphine oxide was filtered off. After removal of the solvent, the liquid residue was subjected to chromatography on a short silica gel column using pentane as eluent to yield the pure (+)-(1*S*,2*S*,5*R*)-menthyl chloride (**3l**) 0.167 g (96%); $[\alpha]_{589} = +57.2$ (c = 1.8, EtOH); ^{1}H NMR ($CDCl_3$) δ 0.896 (dd, J = 6.4 Hz, 6H), 0.938 (d, J = 6.6 Hz, 3H), 4.505−4.517 (m, 1H).

(−)-Cholesterol (2m). To a solution of cholesterol [(0.386 g, 1 mmol; $[\alpha]_{589} = -40.2$ (c = 2.00, $CHCl_3$)] and triphenylphosphine (0.262 g, 1 mmol) in benzene (3 mL) was added dimethydichloroselenurane (**1a**) (0.180 g, 1 mmol) in small portions over 10 min. The reaction mixture was kept at room temperature for 20 h. Then, hexane (10 mL) was added, and triphenylphosphine oxide precipitated was filtered off. The filtrate was concentrated, and the residue was subjected to chromatography on silica gel using hexane as eluent to yield the levorotatory cholesteryl chloride **3m**: 0.340 g (84%); mp 95−96 °C;[15] $[\alpha]_{589} = -31.2$ (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.862 (dd, J = 6.58 Hz, 6H, protons), 0.935−1.209 (m, 11H), 1.025 (s, 3H, 6H), 1.245−1.599 (m, 12H), 1.767−2.082 (m, 6H), 2.441−2.567 (m, 2H), 3.764 (tt, J = 4.75, 6.58 Hz, 1H); MS(CI) 408.3 ($M^+ + 1$ for ^{37}Cl), 406.3 ($M^+ + 1$ for ^{35}Cl), 371.4 ($M^+ + 1 - {}^{37}$Cl and $M^+ + 1 - {}^{35}$Cl).

(+)-(*S*)-[[α-(Trifluoromethyl)benzyl]oxy]triphenylphosphonium Chloride 5. To a solution of (+)-**4** [0.352 g, 2 mmol, $[\alpha]_{589} = +40.8$ (neat)] and triphenylphosphine (0.524 g, 2 mmol) in benzene (10 mL) was added dimethyldichloroselenurane (**1a**) (0.36 g, 2 mmol) in small portions at room temperature over 5 min. During addition of the selenurane, the reaction mixture became cloudy, and soon after, two phases were formed. The solvent was removed, and the oily residue was shaken with petroleum ether (5 mL), which was decanted. The procedure was repeated three times, giving white crystals: 0.802 g (93%); $[\alpha]_{589} = +67.2$ (c = 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 6.433 (dq, J_{H-F} = 5.74 Hz, J_{H-P} = 9.23 Hz, 1H), 7.150−7.800 (m, 20H); ^{31}P NMR ($CDCl_3$) δ 67.03; ^{19}F NMR ($CDCl_3$) δ −76.299 (d, J_{H-F} = 5.74 Hz). Anal. Calcd for $C_{26}H_{21}ClF_3OP$: C, 66.03; H, 4.44; P, 6.56. Found: C, 65.93; H, 4.43; P, 6.39.

(−)-(*R*)-α-(Trifluoromethyl)benzyl Chloride 6. A solution of (+)-(*S*)-**5** (0.645 g, 1.2 mmol) in a mixture of benzene and acetonitrile (1:1 v/v, 20 mL) was heated at 80 °C for 72 h. The progress of the reaction was followed by polarimetry (optical rotation value changed during this period from +1.743 to −1.140). After this time, the solvents were removed by evaporation at reduced pressure (∼20 mmHg). The liquid residue was dissolved in petroleum ether (20 mL) and kept in a refrigerator for 12 h. The organic solution was decanted from the precipitating triphenylphosphine oxide and passed through a short column filled with silica gel in order to remove the last traces of triphenyl phosphine oxide. Removal of the solvent gave the pure levorotatory chloride: 0.52 g (100%); $[\alpha]_{589} = -27.9$ (c = 2.26, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 5.266 (q, J_{H-F} = 6.25 Hz, 1H), 7.364−7.531 (m, 5H); ^{19}F NMR ($CDCl_3$) δ −73.717 (d, J_{H-F} = 6.3 Hz); HRMS-(EI) M^+ calcd for $C_8H_6F_3Cl$ 194.0110, found 194.0118.

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Supporting Information Available: Copies of ^{1}H, ^{19}F, and ^{31}P spectra for compounds **3d**−**g**,**i**,**l**,**m**, **5m**, **6**, and structures **A** and **B** (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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